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(54) **POROUS MATERIAL AND METHOD OF OBTAINING IT.**

(57) A porous polyvinylchloride (PVC) material with a cellular, 5-98 percent cross-linked structure is obtained by aggregation treatment of a powder, emulsion-like, or microsuspension PVC material with subsequent heating at 190-300 °C for 3-15 min. Aggregation treatment includes forming the PVC material at 0.5-400 MPa and 20-170 °C up to a density of 0.85-1.38 g/cm³, or granulation of the PVC material with subsequent separation of the fraction with the size of granules from 0.2 to 4.0 mm and its pressure-free forming in the form of a layer with the height of 4-16 mm.

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FIELD OF THE INVENTION

The invention relates to porous polyvinylchloride (PVC) materials and their production methods.

5 BACKGROUND OF THE INVENTION

It is known, that light porous PVC materials with improved physical and mechanical properties, e.g. high elasticity and thermostability, very often are multicomponent systems, including a number of specially aimed additives: foaming, stabilizing and cross-linking agents, fillers, lubricants, etc. However, introduction
10 of specially aimed additives, which improve some properties, causes worsening of other ones and increase of the materials cost.

There is known a porous material, consisting of PVC without any additive, which is characterized by total porosity of 48-49% and by pore max. diameter of 18-22 microns (The USSR inventor's Certificate No. 651014, C 08 J 9/24/B 29 D 27/08, published in 1979). Reproduction of this material showed, that it has a
15 corpuscular pore structure, characterized by apparent density of 0.72 g/cu.cm, open porosity of 49%, average diameter of open pores of 15 microns, absence of cross-linking (the insoluble fraction amount is zero); its elasticity (measured as a minimal diameter of the roller, around which the material bends without failure) is 35 mm. The material destruction rate under vacuum at 175 °C, which characterizes its thermostability, is $1.25 \cdot 10^{-6}$ mg HCl/g PVC.s. The relation of breaking stress at tension to apparent density is 4.3
20 MPa.cu.cm/g.

From this reference there is known the method of porous material production by molding PVC powder in a cold state by a roller, the lower layer of not treated PVC and upper layer of PVC preliminary thermally treated at 100-150 °C, or the lower and the upper layers of thermally treated PVC and the interfacial layer of not treated PVC, are being applied on the backing with the following heating at 200 °C for 3 mins. or at
25 280 °C for 1 min.

The proximate to the suggested material according to technical concept is the known porous material of PVC (unspecified) containing no additives, characterized by total porosity of 49-50% and pore max. diameter of 25-30 microns, which has elasticity (determined by the above mentioned method) of 30 mm, tensile strength of 3.5-5.0 MPa (The USSR Inventor's Certificate No. 439497, C 08 J 47/08, published in
30 1974). Reproduction of this material showed, that it has a corpuscular pore structure, characterized by apparent density of 0.70-0.72 g/cu.cm, open porosity of 50%, average diameter of open pores of 20 microns, absence of cross-linking (the insoluble fraction is absent). When tested by bending around the rollers of diameter less than 30 mm the material is destroyed, i.e. its elasticity is 30 mm. The material destruction rate under vacuum at 175 ° is $1.20 \cdot 10^{-6}$ mg HCl/g g PVC.s. The relation of breaking stress at
35 tension to apparent density is 4.9-7.0 MPa cu.cm/g.

From this reference there is known the method, which is proximate to the method of the present invention according to technical concept. This known method comprises a preliminary treatment of powder PVC by its heating at 125-130 °C and molding in a free state by a roller on the moving backing, the following heating in a tunnel oven at 180-220 °C, the treatment by water and surfactant solution.

40 The corpuscular noncross-linked porous structure of the described materials provides their relatively low strength and elasticity.

DESCRIPTION OF THE INVENTION

45 An object of this invention is to provide one-component porous PVC material, having an alternative structure and new properties, in particular, improved strength and elasticity.

To achieve this object there are suggested the porous material, which consists of emulsion or microsuspension polyvinylchloride, has cellular porous structure and 5-98% cross-linking extent, and the method of production of the porous material by way of preliminary treatment of powder PVC, followed by its
50 heating above 180 °C, in which emulsion and microsuspension polyvinylchloride is subjected to aggregating treatment, followed by heating at 190-300 °C for 3-15 mins.

It was found, that the preliminary aggregating treatment of powder PVC allows to set in it such structure formations, which in the process of the following heating lead to obtaining of cross-linking porous structures. The presence of such structures provides improved strength and elasticity of the porous material.
55 Simultaneously, its thermostability is being increased.

Improved strength, elasticity and thermostability of the suggested material in comparison with the one-component porous PVC materials of the prior art are conditioned by its distinguishing features: cellular structure and presence of cross-linking. From the prior art it is known, that the materials of cellular structure

at other parameters being equal have higher elasticity than those of corpuscular structure, and cross-linked materials have higher strength than noncross-linked ones. However, it is also known, that cross-linking may cause lowering of elasticity, and strength alteration during transition from corpuscular to cellular structure may be different. Hence it appears, that the prior art does not result in influence of combination of the proposed PVC materials distinguishing features - cellular structure and cross-linking extent - on its strength and elasticity and especially on its thermostability. The porous material of 5% cross-linking extent has low elasticity, and that one of more than 98% cross-linking extent - low thermostability.

DESCRIPTION OF THE ALTERNATIVE EMBODIMENTS OF THE INVENTION

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Depending on what kind of articles are to be manufactured of the proposed material, alternative embodiments of preliminary aggregating treatment are possible.

If the material is intended for production of piece articles of a predetermined shape, it is advisable to carry out aggregating treatment by molding PVC under a pressure of 0.5-400 MPa and at a temperature of 20-170 °C to achieve density of 0.85-1.38 g/cu.cm. In this case aggregating of the powder PVC particles takes place in its full volume, subjected to molding. In the process of further heating PVC attains a cellular porous structure. The material obtained according to this embodiment of the present invention is characterized by a cellular porous structure, having 5-98% cross-linking extent, 0.15-1.20 g/cu.cm apparent density, 0.5-75% open porosity, 1-90 microns average diameter of the open pores, 1-2 mm elasticity, 8.5-33 Mpa.cu.cm/g ratio of breaking stress at tension to apparent density, $0.2-0.8 \cdot 10^{-6}$ mg HCl/g PVC.s. destruction rate under vacuum at 175 °C.

The combination of the material properties in the above given ranges, required for a definite consumer, is achieved due to selection of the material production process parameters within the scope of the present invention.

Realization of this alternative embodiment of aggregating treatment at the temperature of below 20 °C and molding pressure above 400 MPa does not affect the material properties, but requires additional power consumption. Reducing pressure below the claimed value and increasing temperature above the claimed value do not lead to formation of a porous material suitable for application. Molding of the powder PVC, having density below 0.85 g/cu.cm or above 1.38 g/cu.cm, either do not allow to obtain integral material, or leads to obtaining the material having high apparent density and low cross-linking extent.

To obtain the textured surface articles or long-size articles another alternative embodiment is preferred, in which the aggregating treatment includes granulating powder PVC, isolation of the fraction of 0.2 to 4.0 mm diameter granules, its molding in a free state in the form of 4-16 mm thickness layer. In this case the PVC particles aggregation takes place in the process of granules formation, and the processes, proceeding during the following heating of PVC inside the granule and on the surface of their contact, lead to cellular porous structure formation.

The powder PVC granulation, required for the present process realization, may be carried out in any known manner, which provides the PVC particles aggregating, i.e. by mixing at heating or at self-heating (by the powder vibration treating, by extrusion, etc.).

Realization of the embodiment, using the granules size of the layer thickness below the claimed ones, leads to high density material production, and with those above the claimed ones - to obtaining the material unfit for further application (pits, rugged surface etc.).

The obtained material is characterized by a cellular structure, 5-98% cross-linking extent, 0.30-0.80 g/cu.cm apparent density, 1 mm elasticity, and according to its properties it is like the material produced according to the first embodiment of the present invention.

The embodiments described above may be used for production both long-size and piece articles.

PVC heating after the preliminary aggregating treatment is fulfilled in both embodiments at 190-300 °C for 3-15 min. Moreover, as a rule, the heating temperature increase reduces its duration. At the heating temperature and time, which are below the claimed ones, a noncross-linked material of high apparent density (1.25-1.32 g/cu.cm) is formed. The process realization at the heating temperature and time, which are above the claimed ones, does not lead to formation of porous material useful for application.

The material properties, required for a definite user, in the above mentioned ranges are achieved due to the selection of an embodiment and its production parameters in the claimed ranges.

For better understanding of the present invention there are given illustrative examples of its realization.

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Example 1.

Powder emulsion PVC (TU 6-02-69-89) is molded under a pressure $P_{mo} = 0.5$ MPa and a temperature $T_{mo} = 80^\circ$ C. The pelletized material ($d = 10$ mm, $h = 6$ mm), having density $r_p = 0.85$ g/cu.cm, is heated in a free state at an oven temperature $T_h = 250^\circ$ C for $t_h = 6$ mins. A microporous material of cellular structure; determined by optical and electron microscopy methods, is obtained.

The apparent density r_m and the open porosity P_{op} are determined by a hydrostatic weighing; the average diameter of the open pores D_{av} is determined by air forcing through the material of 1 mm thickness. The cross-linking extent as an insoluble fraction amount (P_{it}) is determined by solving in tetrahydrofuran for 24 hrs. at 30° C. The value of breaking stress at tension is determined according to GOST 17370-71 and the ratio of this index to the material apparent density p_b/r_m is calculated. The elasticity (E) of 0.8 mm thickness material is evaluated by the roller of minimal diameter, at bending of which no material destruction occurs. The thermodestruction rate (V_{HCl}) is the amount of HCl, isolated at 175° C under vacuum; per unit of PVC mass in a unit of time.

Table 1 illustrates the working conditions and the material properties according to this and the following examples.

Examples 2-20.

The process is performed according to the procedure of Example 1, the conditions of the material production being changed, thus in examples 2-12 an emulsion PVC (TU 6-02-69-89) is used, in examples 13-15 an emulsion PVC (GOST 14039-78) is used, in examples 16-20 a microsuspension PVC (TU 6-01-1265-81) is used. A porous material of cellular structure is obtained.

Example 21 (Comparative).

Powder emulsion PVC (TU 6-02-69-89) is thermally treated at 130° C in a mixer, then cooled and sieved through sieve No. 55-61 (particle size is 1-100 microns), then it is fed to the second bin of the belt machine for molding. The first bin is charged with the same PVC without thermal treatment. From the first bin PVC is fed to a metal belt, on which a smooth molding roller is located. The molded layer of 0.4 mm thickness advances under the outlet of the second bin, therefrom it comes to the profile roller, which forms the second layer of 0.4 mm thickness and 0.7 mm rib height, after that the double layer enters the tunnel oven, where at 280° C for 1 hr a microporous sheet of corpuscular structure is being sintered. The obtained material is cooled, washed with water, hydrophilized by sulphanoole solution, dried and determined according to its properties.

Example 22 (Comparative).

Powder emulsion PVC (TU 6-02-69-89) is thermally treated at 130° C, and then it is treated by analogy with Example 21, but without forming the layer of not treated PVC, and sintering proceeds at 200° C for 2 mins. A porous material of corpuscular structure is obtained, which then is cooled, washed, hydrophilized and determined according to its properties.

Example 23 (Comparative).

The porous material is obtained by analogy with Example 22, sintering being performed at 250° C for 6 mins., i.e. within the ranges of the suggested method. The obtained material has a corpuscular structure.

Example 24.

Powder emulsion PVC (TU 6-02-69-89) is mixed for 7 mins. in a high-speed mixer ($n = 1,000$ rpm), where the temperature rises to 130° C due to self-heating, then the material is sieved on the sieve with cell size of 0.2 mm and 4 mm, the fraction of 0.2 to 4 mm is molded in 10 mm thickness layer and is heated in the oven in a free state at 250° C for 6 mins. The porous material properties are determined by analogy with Example 1.

Table 2 illustrates the working conditions and the material properties according to this and the following examples.

Example 25.

Powder emulsion PVC (GOST 14039-78) is treated as in Example 24.

5 Example 26.

Powder microsuspension PVC (TU 6-01-1265-81) is mixed for 10 mins. in the preheated screw mixer ($n = 60$ rpm), being maintained at a temperature of 150°C , then the material is sieved, after that a fraction of 0.5-4 mm is isolated and treated as in Example 24.

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Example 27.

Powder emulsion PVC (TU 6-02-69-89) is wetted and subjected to simultaneous granulation and classifying in the system of vibrosieves, the fraction having size of 1 to 2 mm is isolated and treated as in

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Example 24.

Examples 28-29.

Powder emulsion PVC (TU 6-02-69-89) is treated by analogy with Example 24, the granule size, the

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layer thickness and the heating conditions being changed.

COMMERCIAL APPLICABILITY

The porous materials may be produced on commercial scale according to the method of the present invention and may be used as filters, vibration-, sound- and acoustic-proofing materials, applied in civil and industrial engineering, automotive industry, ship-building industry, aircraft industry, etc., as well as in production of various household articles.

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Table 1
Porous PVC material production conditions and properties

| No. of ex. | Molding conditions | | | Heating conditions | | | Properties of the material | | | | | | | |
|------------------|--------------------|-----|---------|-----------------------|------|------|----------------------------|----|--------|----|------|-------------|------------------------|---------|
| | P | T | r | T | t | h | r | P | D | P | E | P | r | V |
| | MPa | °C | g/cu.cm | °C | min. | °C | g/cu.cm | % | micron | % | mm | MPa.cu.cm/g | mg HCl.10 ⁶ | g PVC.s |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | | |
| 1. | 0.5 | 80 | 0.85 | 250 | 6 | 0.37 | 44 | 4 | 83 | 1 | 18.9 | 0.45 | | |
| 2. | 400 | 20 | 1.34 | 250 | 6 | 0.18 | 65 | 3 | 95 | 1 | 16.8 | 0.75 | | |
| 3. | 2 | 170 | 1.30 | 250 | 6.5 | 0.28 | 49 | 5 | 55 | 1 | 14.8 | 0.50 | | |
| 4. | 150 | 20 | 1.32 | 190 | 15 | 0.25 | 54 | 2 | 56 | 1 | 9.1 | 0.50 | | |
| 5. | 150 | 20 | 1.32 | 300 | 3 | 0.36 | 43 | 2 | 83 | 1 | 20.0 | 0.50 | | |
| 6. | 150 | 20 | 1.32 | 250 | 3.5 | 1.20 | 0.5 | 2 | 5 | 2 | 33.0 | 0.80 | | |
| 7. | 150 | 20 | 1.32 | 250 | 5 | 0.35 | 4 | 6 | 56 | 1 | 19.0 | 0.50 | | |
| 8. | 150 | 20 | 1.32 | 250 | 6 | 0.20 | 75 | 18 | 95 | 1 | 9.6 | 0.60 | | |
| 9. | 300 | 20 | 1.32 | 250 | 6.5 | 0.15 | 74 | 6 | 98 | 1 | 9.8 | 0.60 | | |
| 10. | 20 | 20 | 0.98 | 250 | 6 | 0.21 | 61 | 2 | 94 | 1 | 10.4 | 0.55 | | |
| 11. | 150 | 40 | 1.33 | 250 | 6 | 0.19 | 58 | 2 | 87 | 1 | 13.8 | 0.60 | | |
| 12. | 150 | 30 | 1.32 | 280 | 5 | 0.19 | 75 | 4 | 96 | 1 | 8.5 | 0.60 | | |
| 13. | 20 | 100 | 1.38 | 250 | 5 | 0.45 | 36 | 63 | 72 | 1 | 24.0 | 0.45 | | |

Table 1 (continued)

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 |
|---------------|-----|-----|------|-----|-----|------|----|----|----|----|------|------|
| 14. | 150 | 20 | 1.26 | 250 | 4.5 | 0.70 | 20 | 52 | 28 | 2 | 29.0 | 0.30 |
| 15. | 150 | 20 | 1.26 | 250 | 5 | 0.45 | 37 | 90 | 72 | 1 | 23.1 | 0.45 |
| 16. | 0.5 | 170 | 1.20 | 300 | 3 | 0.46 | 33 | 4 | 57 | 2 | 22.0 | 0.45 |
| 17. | 400 | 20 | 1.36 | 190 | 15 | 0.22 | 49 | 3 | 73 | 1 | 10.3 | 0.55 |
| 18. | 150 | 20 | 1.32 | 240 | 4.5 | 0.89 | 24 | 3 | 42 | 2 | 21.0 | 0.20 |
| 19. | 150 | 20 | 1.32 | 250 | 4 | 0.89 | 1 | 1 | 42 | 2 | 30.8 | 0.20 |
| 20. | 150 | 20 | 1.32 | 250 | 6.5 | 0.20 | 54 | 5 | 87 | 1 | 10.1 | 0.55 |
| 21. | - | - | - | 280 | 1 | 0.72 | 49 | 15 | 0 | 35 | 4.3 | 1.25 |
| (comparative) | - | - | - | 200 | 2 | 0.70 | 50 | 20 | 0 | 30 | 7 | 20 |
| 22. | - | - | - | 250 | 6 | 1.26 | 8 | 3 | 2 | 20 | 15 | 40 |
| (comparative) | - | - | - | - | - | - | - | - | - | - | - | - |
| 23. | - | - | - | - | - | - | - | - | - | - | - | - |
| (comparative) | - | - | - | - | - | - | - | - | - | - | - | - |

Table 2

Porous PVC material production conditions and properties

| No. of ex. | Granule size, mm | | Thickness of layer, mm | Heating conditions | | Properties of the material | | | | | |
|------------|------------------|-----|------------------------|--------------------|----------|----------------------------|--------|------|----------------------------------|------------------------------|--|
| | from | to | | T °C | t h min. | r _m g/cu.cm | P if % | E mm | p / r _{b m} MPa.cu.cm/g | V HCl mg HCl.10 ⁶ | |
| | | | | | | | | | | | |
| 24. | 0.2 | 4.0 | 10 | 250 | 6 | 0.70 | 5 | 1 | 15.0 | 0.30 | |
| 25. | 1.0 | 1.6 | 4 | 250 | 5 | 0.80 | 3 | 1 | 15.3 | 0.40 | |
| 26. | 0.5 | 4.0 | 8 | 250 | 8 | 0.46 | 46 | 1 | 14.6 | 0.50 | |
| 27. | 1.0 | 2.0 | 8 | 190 | 15 | 0.40 | 51 | 1 | 12.6 | 0.50 | |
| 28. | 1.0 | 2.0 | 8 | 300 | 3 | 0.30 | 80 | 1 | 10.0 | 0.55 | |
| 29. | 0.5 | 4.0 | 16 | 250 | 12 | 0.37 | 65 | 1 | 12.3 | 0.55 | |

Claims

1. A porous material, consisting of emulsion or microsuspension polyvinylchloride, characterized by a cellular porous structure and 5-95% cross-linking extent.

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2. A process for porous material production, comprising a preliminary treatment of powder emulsion or microsuspension polyvinylchloride and its following heating at a temperature of above 180 ° C, wherein polyvinylchloride is subjected to an aggregating treatment and then it is heated at 190-300 ° C for 3-15 mins.

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3. A process as claimed in Claim 2, characterized in that the aggregating treatment comprises molding of powder polyvinylchloride under a pressure of 0.5-400 MPa and at a temperature of 20-170 ° C to achieve 0.85-1.38 g/cu.cm density.

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4. A process as claimed in Claim 2, characterized in that the aggregating treatment comprises granulating of powder polyvinylchloride, isolation of fraction of 0.2 to 4.0 mm granules and its molding in a free state as a layer of 4-16 mm height.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/RU 93/0089

A. CLASSIFICATION OF SUBJECT MATTER

IPC⁵ C08J 9/24/(C08J 9/24, C08L 27:06)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC⁵ C08J 9/24, C08L 27/06

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| A | US,A,3438912 (HIROSHI TSUKAMOTO et al.), 15 April 1969 (15.04.69) | 1-4 |
| A | US,A,3349046 (JERROLD J.ABELL et al.), 24 October 1967 (24.10.67) | 1-4 |
| A | SU,A,90375 (Leblein Fridrich et al.), 31 January 1951 (31.01.51) | 3 |
| A | SU,A1,1643570 (Vladimirovsky khimichesky zavod et al.) 23 April 1991 (23.04.91) | 3 |
| A | SU,A,912738 (Sverdlovsky zavod plasticheskikh mass) 15 March 1982 (15.03.82) | 4 |
| A | DE,A1,1290335 (SUMITOMO CHEMICAL COMPANY LTD.) 06 March 1969 (06.03.69) the claims | 4 |

☒ Further documents are listed in the continuation of Box C.☐ See patent family annex.

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|---|--|
| * Special categories of cited documents: | "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention |
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19 July 1993 (19.07.93)Date of mailing of the international search report
11 August 1993 (11.08.93)

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